A Brief History of the OAS Low Energy Plasma Radiocarbon Sampling Laboratory

The use of low energy plasmas to generate radiocarbon samples was pioneered in 1990 by Dr. Marvin Rowe and colleagues (Russ et al. 1990, 1991) at Texas A&M University (TAMU). Subsequent research and experimentation with TAMU graduate students, supported in part by an NCPTT grant, eventually resulted in two laboratories being founded, one under the direction of Dr. Ruth Armitage (Eastern Michigan University) and the other under the direction of Dr. Karen Steelman (University of Central Arkansas, now at the Shumla Institute, Comstock, Texas). Dr. Rowe retired to Santa Fe, New Mexico, and he approached the Conservation Bureau and the Office of Archaeological Studies (OAS) divisions of the Museum of New Mexico with an offer to collaborate in the construction of another laboratory. That collaboration was initiated in January 2013 with the installation of the first equipment in OAS laboratory space at the then newly completed Center for New Mexico Archaeology in Santa Fe, New Mexico.

The core of the laboratory is a surplus NASA mass spectrometer that Rowe had obtained through the surplus property program at TAMU. The mass spectrometer was reconfigured and augmented with equipment Rowe had accumulated through years of teaching and research. Beginning in 2014, OAS and Conservation provided access to funding through the newly established Dr. Don E. Pierce Endowment for Archaeology and Conservation (Pierce Fund), administered by the Museum of New Mexico Foundation (MNMF). The development team consists of Rowe, OAS staff (Eric Blinman, Director, and Jeffrey R. Cox, Laboratory Technician), Conservation staff (Mark MacKenzie, Director) and volunteer John Martin (retired physicist and instrumentation specialist). Joe Martin (retired chemist) participated as a volunteer consultant for residual gas analysis (RGA) in 2016. Through MNMF, OAS applied for and received a National Center for Conservation and Preservation Technology grant in 2015 which carried through September of 2016. This report summarizes the status of the laboratory and the plasma radiocarbon sampling process, including results of experimental sampling and substantive improvements that were initiated and accomplished during the grant period.

Overview of Radiocarbon Sampling

Radiocarbon dating can be accomplished by accelerator mass spectrometer (AMS) measurement of carbon isotope ratios with as little as 40-100 micrograms of carbon (μg, or millionths of a gram). Organic materials are usually in equilibrium with the carbon isotope ratios in the environment, and the ^{14}C radioactive content of the atmosphere is constantly being renewed by cosmic ray bombardment of the upper atmosphere. The half-life of ^{14}C is relatively short (about 5,730 years), and the ratio of ^{14}C to other isotopes decreases with the amount of time an organism has been isolated from the atmospheric pool (after death). Isotope ratios, measured by AMS analysis, can be used to estimate the time since death in radiocarbon years before the present (1950). Isotope measurement error is reflected in one-sigma or two-sigma error terms that are calculated with the radiocarbon date. Radiocarbon age calculations assume a constant equilibrium ratio in the atmosphere, but the atmosphere ^{14}C ratio varies slightly from year-to-year and across longer time periods, and that variation has been calibrated by analyzing the isotope rations in dated tree-ring series. Radiocarbon dates are reported as the isotope ratio-based age (years BP) and its error (± years that represent either one or two sigma confidence intervals, 68 or 95 percent probability that the true age falls within the ± range) and as a calibrated age range (Cal) through comparison with current tree-ring calibration programs. Where BP error probability are described by a normal curve, calibration error probabilities are more complicated and are often expressed as graphs where the x-axis is time and the y-axis reflects the probability that the observed carbon isotope ratio of the sample could be the result of the accumulation of carbon at that time.

Although only as little as 40 μg of carbon are needed for AMS radiocarbon dating, traditional approaches to selecting and submitting archaeological samples require much larger amounts of source material: 2-5000 mg or 40 to >100,000 times the mass of carbon actually needed for a single isotope measurement. The large sizes for traditional AMS samples are determined by the amount of carbon within the material and need for pretreatment protocols that remove contaminating carbon that either pre- or post-dates the carbon of interest. These contaminants are in the form of carbonates, oxalates, and humic acids that can accumulate within archaeological materials depending on their depositional history. Carbonates and humic acids are routinely removed in pretreatment, but oxalate contamination is still under study (Hedges et al 1998). Routine contaminant removal is generally accomplished with acid-base-acid pretreatments that are chemically and physically harsh and that result in the loss of large proportions of the original sample material. Remaining sample material is then converted to graphite which in turn is submitted for AMS isotope measurement. Traditional approaches to AMS radiocarbon sampling are therefore destructive, and the amount of material destroyed or damaged varies with the type of material to be dated.

Low Energy Plasma Oxidation Sampling

Low energy plasma sampling collects carbon for radiocarbon dating in the form of carbon dioxide gas (CO_2) by oxidizing organic molecules from the surface of the object or material. Potentially contaminating humic acids must be removed from the surface by pretreatment, but the plasma energy is kept below the threshold at which carbonates and oxalates are oxidized, and pretreatments for those contaminants are unnecessary. Humic acids can be rinsed away with a mildly alkaline (pH 8.0) buffer solution (Armitage et al. 2012), which requires wetting and drying the sample, but otherwise no physically observable portion of the sample needs to be destroyed. The energy of the plasma can be controlled during sampling, and lower energies (5 watts or less of radio frequency energy) result in sampling at temperatures of 40° C (104° F) or less. The entire material or object to be dated can be sampled, or a portion can be removed and sampled, or portions can be masked and the remainder sampled, but in many cases the sampling process can be viewed as "non-destructive" of the material or object. The only practical limitation on plasma sampling is the size of the sampling chamber which must accommodate the object. Alternatively, extremely small amounts of material can be removed from an object (it has to be visible for manipulation but it only has to contain circa 100 μg of surface-accessible carbon). Plasma sampling also can be carried out in "destructive mode," meaning that higher energy plasmas can be applied (still below the oxidation threshold of carbonates and oxalates), and the plasma oxidation can be carried out until all accessible carbon has been oxidized.

Detail of the CNMA Low Energy Plasma Sampling Process

The sampling process consists of intake and assessment, pretreatment if needed, plasma oxidation, and submittal of the completed sample for AMS dating. The protocol for any individual sample depends on the nature of the material to be dated, and the goals or constraints defined by the submitter. Potential variations in protocols are wide, and a single real example will be used here to illustrate the process.

Assessment

The archaeologist (Regge N. Wiseman) was attempting to date a Formative site in southern New Mexico that had been tested but not fully excavated. The limited pottery types from the excavations provided inconclusively wide date ranges, a single tree-ring sample collected from upper levels was not datable but did result in a modern radiocarbon date, and no other samples suitable for standard radiocarbon dating had been collected during the excavations. Cooking jar sherds with creosote accumulations (cooking soot) were part of the excavated collections, and two sherds were requested on loan from the Archaeological Research Collections of the Museum of Indian Arts and Culture. Destructive analysis was permitted in the granting of the loan request. The description here applies to one of the two sherds, identified as 4-34B.

The sherd provided an opportunity to explore, within the framework of the NCPTT grant, different approaches to the application of plasma sampling. The sherd was photo-documented and broken into subsamples. One was retained as an unmodified voucher, one sherd was to be sampled with the plasma technique, and one sherd was to be scraped so that creosote residue could be dated independently of the sherd. Humic acid contamination was possible based on the archaeological context, so pretreatment with a pH 8 buffer solution was indicated for the two non-voucher sherd specimens.

Pretreatment and Sample Preparation

The two specimens from 4-34B were pretreated together. They were placed in a small beaker and pH 8 phosphate buffer solution was added to cover the specimens. The beaker was ultrasonicated to aid penetration of the buffer solution. The solution was light yellow, indicating the presence of a low concentration of alkaline-soluble organic compounds, and the sherds were subjected to a total of 12 cycles of pH 8 rinses until the solution was very very pale. Distilled water rinses followed. The first rinse was clear, the second DH_2O rinse was brown, and subsequent rinses lightened in color. Eight DH_2O rinses were completed before the last rinse was clear, and the sherd specimens were dried at 45° C. One sherd specimen was held in the oven for plasma sampling ("sherd"), and the other specimen was carefully scraped under binocular microscope observation, removing and retaining only the adhered soot ("creosote"). The creosote scrapings (dust) were transferred to a kiln-cleaned porcelain "boat" (see Appendix 1). The sherd specimens could have been dried at 145° C, since destructive sampling had been authorized.

The sherd specimen to be sampled was placed into a cleaned sampling chamber, and the chamber was attached to the plasma sampling system (see the physical description of the "system" and its parts below). The porcelain boat with the creosote powder was placed into a second chamber and attached to the sampling system. The chambers were evacuated to a pressure of 10^{-6} torr (atmospheric pressure is 760 torr). This evacuation removes most atmospheric gases from the sampling chamber, including modern CO_2 which would be a dating contaminant in the plasma sampling method. CO_2 molecules are "sticky" in that they adhere to (are adsorbed by) chamber and object surfaces, and porous objects can contain residual absorbed CO_2 even under high vacuum. Research grade argon was introduced into the chamber at low pressure (circa 1 torr), and a plasma was generated by applying radio frequency (RF) energy via electrodes that are outside of the chamber. The energized argon plasma species kinetically scour the sample and the chamber surfaces, dislodging adsorbed CO_2 molecules. The warmth of the plasma (40° C or greater in destructive mode) encourages the off-gassing of remaining absorbed CO_2 molecules. At least four argon plasmas of at least 15 minutes duration are applied to the sample, evacuating the chamber to 10^{-6} torr between plasmas. A fifth argon plasma, usually of 30 minutes duration, is then applied while a liquid nitrogen (LN_2) cold trap is in place. The trap sequesters CO_2, water, and occasional trace amounts of other gases by condensing them on the inside of the cold trap at -196° C. Evacuation is completed with the cold trap in place, and the system is then closed. The cold trap is removed (it can be replaced with an ethanol- LN_2 slush trap if there is a need to discriminate water from CO_2 partial pressure), and pressure changes are used to assess whether any significant amount of atmospheric CO_2 is still being evolved from the sample. If CO_2 is detected in amounts that could contaminate a radiocarbon date (0.5 μg or more), argon cleaning plasma cycles are resumed. Gas composition can be examined by RGA if any anomalous conditions are suspected. If less than 0.5 μg of adhering or absorbed carbon is detected, the sample and chamber are clean enough that oxidation can be initiated to create the radiocarbon sample.

Sampling is initiated by introducing research grade oxygen into the chamber at low pressure (1 torr). A plasma is generated by applying radio frequency (RF) energy via electrodes. RF energy is usually in the range of 5 to 20 watts, with associated chamber temperatures of 40° C or lower. Plasma duration necessary to oxidize sufficient carbon for a radiocarbon date is determined by the molecular composition

of the object surface, by the surface area exposed to the plasma, and by the energy of the plasma. Sufficient CO_2 for a radiocarbon date can be generated in as little as 2 minutes of plasma exposure or as much as an hour of exposure. An LN_2 trap is applied during the plasma oxidation to sequester most of the oxidation products (dominated by CO_2 and water), and pressure changes are monitored to estimate the amount of CO_2 being generated. Plasma oxidation is terminated when sufficient CO_2 is believed to have been generated. An ethanol-LN_2 slush trap (circa -90° to -114° C) is substituted for the LN_2 trap (-196° C), and the LN_2 trap is moved to a 4 mm diameter glass sample collection tube. The warmer ethanol-LN_2 slush trap releases CO_2 from the first trap while continuing to sequester H_2O, and the released CO_2 from the sample is recaptured within the glass collection tube. Pressure is monitored to ensure adequate CO_2 has been captured for a radiocarbon date, and the glass tube is flame-sealed above the LN2 to form an ampule that can be detached from the sampling system. All of the carbon in the form of CO_2 in the ampoule will have been derived from the object. The ampule is shipped to the Ion Beam Laboratory at ETH Zürich, the CO_2 gas is flushed directly into their AMS system for isotope measurement, and the radiocarbon age can be calculated from the isotope ratios. From the point that the ampule is sealed, the sample is no different in potential from a standard graphite AMS radiocarbon dating sample.

In this example, two radiocarbon samples were collected from the sherd specimen, and a single radiocarbon sample was collected from the creosote in the porcelain support. ETH Zürich reports the amount of carbon analyzed by AMS for comparison with the estimated amount generated by the plasma sampling. The system pressure gauges (Pirani and cold cathode) and the known volume of the armature are the basis for the OAS estimate, but the pressure gauges are relatively imprecise (within ±30 percent), so perfect correlation is not expected. If there is a serious discrepancy between the estimated submittal and the measured amount, contamination is a possibility.

Table 1. Radiocarbon data for samples from LA 5380								
Sample	OAS Number	Time (min)	RF Power (watts)	OAS Estimated Sample Size (µg C)	ETH AMS Number	ETH Sample Size (µg C)	^{14}C Date (years BP)	Calibrated 2σ Age (AD)
Sherd 5-2	160927d-1	60	10	40	73904.1.1	80	985 ± 65	950-1210
Sherd 5-2	160928d-1	40	25	30	73905.1.1	44	1000 ± 75	890-1210
Creosote 5-2	161017c-1	60	10	60	73908.1.1	67	1575 ± 60	380-610

In this example, there is close agreement between the radiocarbon dates from the two samples oxidized from the sherd specimen, but the scraped creosote yielded a significantly earlier radiocarbon date. There are no methodological explanations for the discrepancy (potential sources of contamination associated with OAS laboratory procedures would produce younger rather than older dates), but it is possible that creosote would carry an "old wood" effect if different fuel types contributed to the creosote accumulation or that scraping could inadvertently include carbon derived from components within the clay body of the sherd that would not be included in the surface oxidation samples.

The OAS Low Energy Plasma Radiocarbon Sampling System

The OAS system for generating and collecting radiocarbon samples consists of a number of interrelated physical and functional components. These components include equipment necessary to achieve and maintain a high vacuum, and the plumbing configuration that applies, controls, and monitors vacuum status and gas movement. An argon and oxygen gas handling system allows rapid and convenient access to gases for cleaning and oxidizing samples. Sampling chambers are available in different sizes, are interchangeable, and up to five can be attached to the system at any one time. Plasmas are generated and

controlled by a radio frequency (RF) generator, a tuner, and electrodes of various forms. A system cold trap segregates gases at various stages in cleaning and sampling, and the sample collection manifold allows the sequential collection of multiple radiocarbon samples from a single chamber. Finally, the appended RGA allows selective characterization of gases released during both cleaning and oxidation phases of radiocarbon sampling.

The NCPTT grant allowed considerable refinement of system architecture through the grant period, including establishing redundant vacuum capacity, creating new chambers for larger samples, improving the efficiency of cleaning multiple chambers simultaneously, adding RGA capability, and improving the handling of cold traps and sample ampules.

The High Vacuum Architecture

The high vacuum architecture consists of a fore pump to initiate the vacuum (down to 10^{-2} torr) and two fore pump-turbo pump combinations to reduce the pressure of the system to approximately 10^{-6} torr. A third fore pump-turbo pump combination is associated with the RGA and can be used to reduce or maintain the high vacuum as needed. The system can function with a single turbo pump, but running two pumps simultaneously decreases the time needed to achieve vacuum thresholds and provides an internal back-up should one vacuum pump fail. All-metal valves isolate areas of the system that are directly exposed to plasmas, and multiple Pirani-cold cathode sensors are used to measure pressures within various portions of the system.

A central manifold supports the sampling chambers and provides access to "services" for each of the sampling chambers in turn or simultaneously. The central manifold is directly connected to vacuum pumps along with valves and pressure sensors that can isolate and control gas movement and evacuation through the various services available to the system: plasma sampling chambers, gas supplies, gas buffer, cold trap, sample collection manifold, and RGA.

The sampling chambers are glass cylinders that can be attached to the high vacuum system. The most commonly used chamber sizes are circa 3.5 cm diameter and 12 cm long. Smaller chambers (circa 1cm diameter and 10 cm long) are available but are rarely used, and the largest chamber currently available circa 9 cm diameter and 38 cm long. Five chambers can be connected to the system at the same time, and at least four can be used simultaneously for cleaning operations (either with argon or oxygen plasmas). Only single chambers can be used when cold traps are needed.

An opportunity arose during the grant period when we were informed that a mass spectrometry lab was being closed at the University of Minnesota. Using Foundation funds for travel and NCPTT grant funds for 6 days of staff time, an OAS staff member and two volunteers drove to Minneapolis and disassembled and packed what is estimated to be $100,000 in surplus high vacuum equipment. The equipment included stainless steel plumbing fixtures, vacuum pumps, valves, an RGA, and tools. This infusion of equipment allowed a reconfiguration of the entire high vacuum system for greater layout efficiency, provided redundancy in vacuum generation, and has eliminated any significant down time for system maintenance.

RF Energy and Plasma Generation

Radio frequency (RF) energy is provided by a controllable generator, is passed through a tuner, and is delivered by double insulated wires to electrodes at the chambers. The generator determines the power of the RF energy delivered to the electrodes, while the tuner is used to modulate the power to reduce or eliminate the inefficiency of reflected energy. Energy is distributed to the chambers after it emerges from the tuner, and apart from the indirect indication of chamber temperature, there is at present no means of quantifying the RF energy that is actually delivered to the electrodes of each individual chamber when

multiple chambers are operating simultaneously. RF energy passes along rather than through conductors, with a positive and a ground conductor. Solid copper (gauge 12 or 14) wires with standard insulation are passed through polyethylene airline tubing for a second layer of insulation. Each new system wiring configuration must be monitored for shorts (proximity to, rather than strictly contact with, grounded objects or surfaces) to prevent overheating of the RF energy system components.

Three types of electrodes are in use on the OAS system: bands, rings, and bars. Copper or brass straps are used to form band electrodes. The bands are placed in direct contact with the glass of the sampling tubes. Width of the bands can be varied, with wider bands conveying greater energy to the plasma as measured by plasma temperatures. Tubular ring electrodes (brass) are slightly larger in inside diameter than the outside diameter of the glass chambers. The chambers are centered within each ring. If the brass of an electrode directly touches the glass of the sampling chamber it presents a risk of blowing a hole in the chamber wall, and polyethylene tubing shields the ring electrodes from direct contact. Bar electrodes are also made of brass, and they are also shielded with polyethylene tubing to minimize risk of chamber damage. In all cases, higher RF energy levels pose a greater threat of damage to system components through shorting. In some cases we have generated plasmas in chambers without electrodes but just through the differential energy of wires that have run adjacent to chambers.

RGA Capability

Theoretical models of plasma oxidation are relatively straight forward, but observations during sampling have suggested that reactions are more complex. Dr. Joe Martin proposed adding an RGA to the system in an effort to monitor gas composition in real time during sample processing, and he loaned an RGA and its software to OAS on a trial basis. The RGA allowed us to examine changing gas composition during sampling, correlating changing system pressures and plasma colors with progressive changes in the oxidation environment of the samples. When the Minnesota RGA became available, it was placed in the system and Dr. Martin's RGA was returned.

The most important study that was initiated during the grant period and that is still underway is the investigation of the role of water vapor during the argon plasma cleaning stage of sample processing. The warming effect of the argon cleaning plasmas commonly releases water vapor, absorbed or lightly bound, and the RF energy creates a combined argon and water plasma. Where an argon plasma alone is non-reactive, water dissociates into hydrogen and oxygen species, and oxidation reactions can take place on the sample surface. The oxidation reactions prematurely begin to produce CO and CO_2 that derive from the hydrocarbon molecules of the sample, making it appear that the sample has not yet been cleaned of adsorbed CO_2. There is also a possibility that lightly bound water within the sample can carry contaminating atmospheric CO_2. We are currently designing experiments that will explore the effect of water vapor on the validity of the CO_2 samples for dating in some circumstances.

Dating Calibration

Plasma oxidation is a sufficiently different approach to preparing radiocarbon samples that calibration with international standards is an important responsibility of the lab. The results of the calibration efforts have been mixed and are suggestive of the need for further research. Selected results are discussed here.

TIRI Wood (Belfast Pine)

Prior to the NCPTT grant, the OAS laboratory had prepared and dated four samples from the TIRI Belfast pine standard. Three additional calibration samples from the standard were submitted during the grant period, and the results of all of the samples are portrayed in Figure 1.
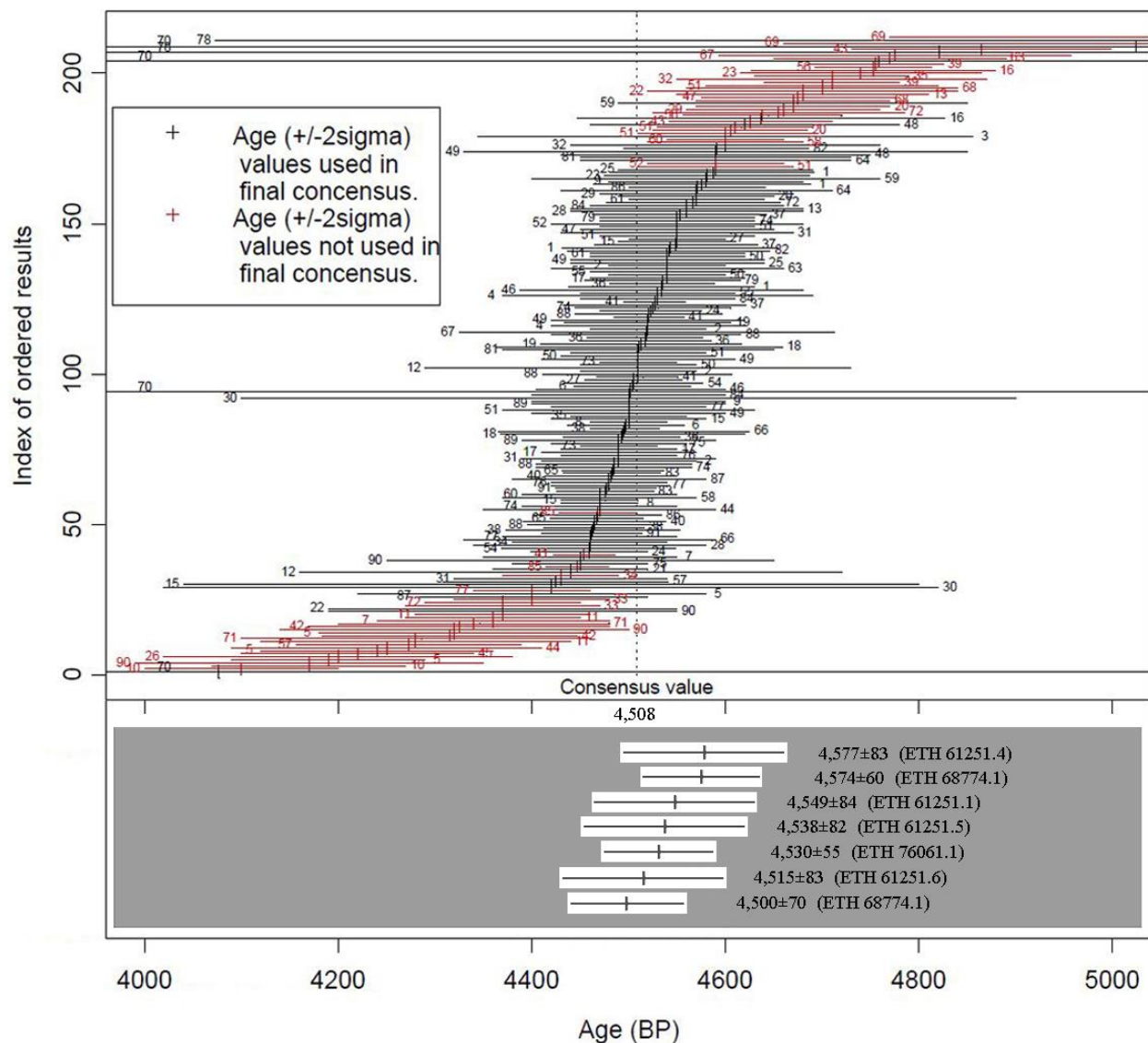
Figure 1. Dating results of OAS plasma samples of the TIRI Belfast Pine standard. The consensus value of all isotope measurement techniques is 4,508 BP, while the mean value for AMS isotope measurements is 4,530±8 BP. The average of the OAS samples is 4,540±30 BP, slightly older that the AMS consensus but well within the range of other radiocarbon laboratories.

These dates are on plant cellulose (wood) and associated resins, and plasma oxidation provides a dating alternative that is consistent with other international radiocarbon dating services.

VIRI R Murex

Plasma oxidation samples of the VIRI Murex standard reveal both strengths and weaknesses of plasma oxidation sampling. The initial preparation and sampling of the murex consisted of a pH 8 rinse to clean a fragment of the shell, followed by standard plasma sampling. The resultant radiocarbon dates were 1,828±65 and 2,850±68 BP compared with the consensus age of 2,491 BP. This sample was processed prior to our understanding of the susceptibility of plasma oxidation samples to surface contamination (see contamination discussion later in this report), and the younger ages could have been determined by a

small amount of inadvertent contamination. An alternative complication is that all of the other radiocarbon laboratories had dated the carbonate component of the shell, while the plasma oxidation sample only dated any proteinaceous material remaining on the shell surface.

In order to investigate the possibility that very different age materials were being dated, a specialized chamber was constructed for the OAS system. Lightly crushed fragments of the murex standard were cleaned and placed in a clean and deep porcelain sample support. After a purge of the chamber, argon was allowed to flow into the chamber at slightly more than atmospheric pressure. An access port to the chamber was opened, and the positive pressure of the argon prevented atmosphere from entering the chamber. HCl was pipetted onto the shell and into the porcelain basin, and the CO_2 generated by the acid-carbonate reaction was captured by a LN_2 trap. The LN_2 trap was isolated from the acid reaction chamber, the system was vacuum purged, and the CO_2 was released while sequestering water in an ethanol slush trap. Three samples of CO_2 from the shell were captured in ampoules with LN_2 and were submitted for dating. The resultant dates were 2,228±56, 2,349±53, 2,400±56, and 2,550±54 BP, for an average carbonate date of 2,382 BP. The OAS carbonate date is only slightly younger than the consensus age of 2,491 BP from the other radiocarbon dating laboratories.

The age discrepancy between the plasma and carbonate dates reflects the different source and type of carbon that is oxidized during plasma sampling. This may be due to inadvertent contamination of the sample during OAS laboratory handling or handling prior to the murex material arriving at OAS. But it is also possible that the proteinaceous component of the shell will ultimately yield a different radiocarbon age than the carbonate component of the shell.

Additional plasma sampling of the VIRI R murex standard is planned, exploring alternative cleaning options so that we can eliminate handling contamination as a concern.

VIRI I Whalebone

Bone radiocarbon dates are also complicated by the option to date collagen or carbonate and by the potential for diagenetic replacement of old carbon with carbon of different age during the time between death of the animal and radiocarbon dating. Two plasma radiocarbon samples were collected from a cleaned VIRI I whalebone sample. The two OAS plasma sample dates were 7,245±82 and 7,250±84 BP. Although these are internally consistent, the consensus age for VIRI I is 8,331 BP, well outside of the error term of the OAS dates. OAS resampled the whalebone using the acid-carbonate reaction, and two CO_2 samples were captured and dated. The dates of 5,697±59 and 5,770±82 were again internally consistent but are not in agreement with other laboratory dates on this standard. More work needs to be done to understand bone sampling in a plasma oxidation environment.

Non-Destructive Sampling

During the development of the OAS laboratory, a modern turkey feather was placed in a chamber and was used to evaluate the effects of plasma oxidation on delicate materials. The result of that exercise is depicted in Figure 2. The lack of damage was remarkable, although we were able to seriously damage the feather at higher plasma energies and temperatures.

The initial feather assessment was a pilot effort, and a more carefully controlled experiment was designed. A fresh segment was cut from a modern turkey feather. The feather was documented both by OAS and by Mark MacKenzie of the Conservation Bureau of the NM Department of Cultural Affairs. The conservation laboratory has much higher quality documentation capability than OAS and would be able to detect subtler impacts of the plasma oxidation exposure on the feather.
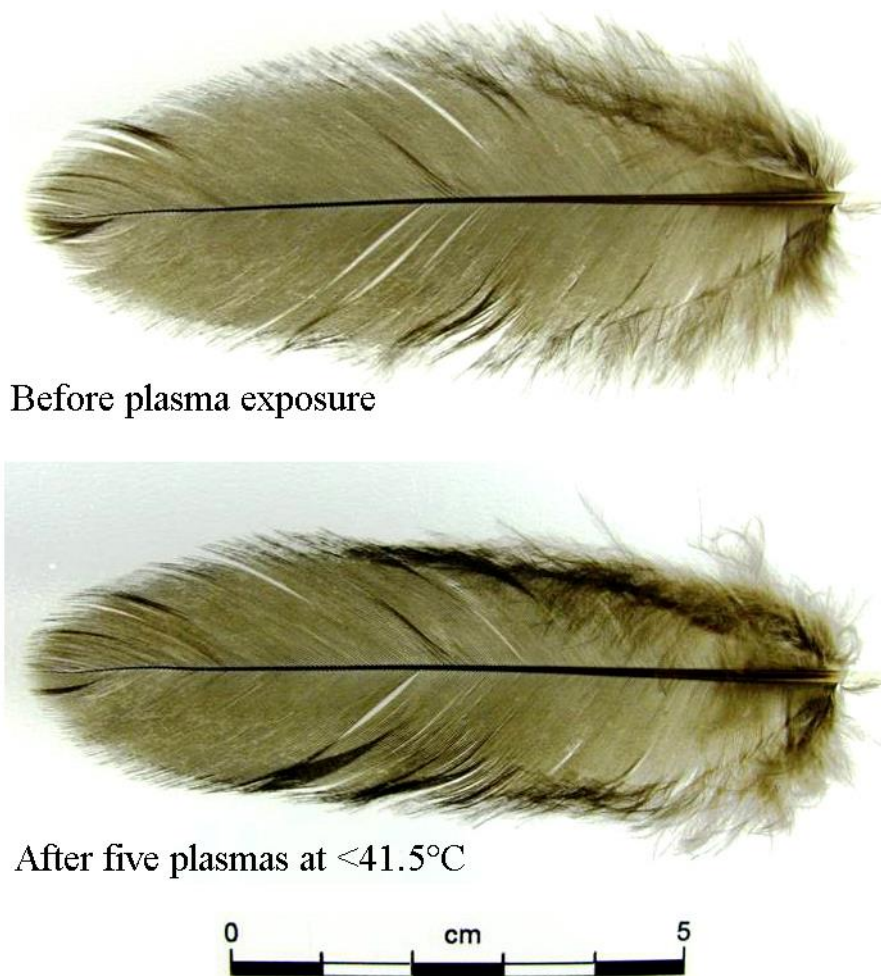
Figure 2. Images of a modern turkey feather before and after plasma oxidation exposure. Multiple radiocarbon samples-worth of CO_2 were generated during the oxidation runs.

The new feather test was conducted on a cut segment of feather (Figure 3). The feather was cut so that its small size would allow placement within, and withdrawal from, a plasma chamber without physical contact between the feather and the chamber mouth. The feather was photo-documented at OAS and then transmitted across town to the conservation lab for their pre-sampling documentation. After the return of the feather, it was prepared for sampling as if it were a normal dating sample. The feather was placed in the chamber, the chamber was evacuated to 10^{-6} torr, and then the feather was exposed to four argon cleaning plasmas per normal sampling procedure. After argon plasma cleaning, sampling proceeded with a two minute plasma oxidation at 5 watts that yielded an estimated 166 µg of carbon (the carbon was not retained).

After sampling, the feather was documented at OAS and turned over to the conservation laboratory for a more careful assessment. Their post-sampling images are presented as Figures 4, and 5. Mark MacKenzie's conservation narrative that accompanied the image transmittal is included here:

Figure 3. OAS pre-plasma documentation image of modern turkey feather segment.

Figure 4. Post-plasma sampling image of downy feather components.

Figure 5. Close-up of downy feather element after plasma sampling.

> I examined the surface and physical construction of the afterfeathers at high magnification and see no change at all. I wasn't able to find and reimage exactly the same spot on the afterfeather but they all look the same and I believe these two images show no physical change in what are extremely fine as in small details. Now please remember that the surface volume to cross section ratio increases greatly as cross section diminishes. This means that the very fine structures of the afterfeathers experience a much greater bombardment/exposure during the plasma treatment than do larger/greater cross sectional areas of the main feather. Thus these afterfeather shaft structures should be the first to show major changes due to plasma and as far as I can determine they do not.
>
> Mark MacKenzie, 9/14/2017

The implications of this experiment are that the OAS laboratory can manipulate some materials within the plasma oxidation radiocarbon sampling process with an effectively non-destructive result.

Masking

Plasma oxidation is a surface preferential technique. The degree of penetration of the energized oxygen plasma species into the surface or crevices of a sample is unknown, but our model of how the process proceeds suggests that the chemical oxidation is dominantly a surface process. If that model is correct, we should be able to mask off portions of an object to exclude those portions from contributing to the

radiocarbon sample. Various options are available for masking, including aluminum foil, but we have yet to find an effective test of the risk of penetration of the plasma species beneath the foil. Another option we have explored is the embedding of samples within a matrix of powdered alumina. The alumina can be kiln-cleaned to eliminate contamination risk, and the fineness of the powder provides a conforming mantle over areas of the sample that need to be excluded from contact with the plasma.

We have used the alumina several times, but only one case was a formal test of the effectiveness of the mask and the results are inconclusive. We buried a dead-carbon wood standard (VIRI K) under the powder with the TIRI Belfast pine exposed to the plasma. After standard sampling protocol, the resulting date was 4,758±61 BP, older than expected by nearly 200 years. This is significantly older than our other TIRI assays, and the implication is that the masked dead carbon contributed 2.6 percent to the sample.

Although this appears to be a failure of the masking approach, the mass of alumina was fissured, and the fissures may have allowed the plasma species to reach the underlying wood. Since this test, we have experimented with other techniques for using the powder that have not fissured, and we will repeat the test again in the near future.

Sampling Organic Painted Pottery

One use of alumina powder masking that may or may not have been successful has been an attempt to collect a radiocarbon dating sample from a Biscuit Ware sherd. This ware was decorated with plant syrup designs before firing, and during firing the hydrocarbons that had soaked into the fabric of the unfired vessel turned to carbon black within the vessel wall. The age of the carbon in the plant syrup would be close to the age of the making of the vessel. A specimen was cut from a larger sherd so that only the black painted surface was exposed on the face of the sample. The specimen was nestled into pile of alumina powder within a porcelain "boat," and the powder was compacted against the edges of the specimen so that only the painted surface was visible (exposed to the plasma).

Biscuit ware pottery was made between perhaps AD 1350 and 1550, and the technological features of this sherd place it within the early portion of that range. Two ampules/dates failed for reasons that are unknown, but one date was 495±57 BP (Figure 6).
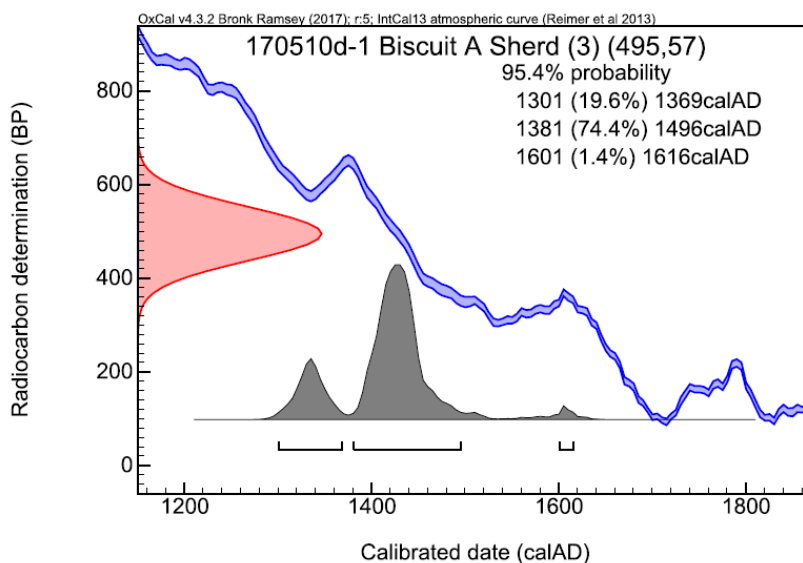

Figure 6. Calibration of the single successful Biscuit Ware radiocarbon date.

The calibrated date falls within expected range for the early Biscuit Wares, but more research will be needed to rule out any contribution to the carbon of the date from carbon that was part of the vessel paste or that was part of contaminating residues.

Extremely Small Samples

The efficiencies of plasma oxidation allow the sampling of many materials without any significant pretreatments, which narrows the gap between the amount of carbon actually needed by the AMS laboratory for radiocarbon dating and the amount of material that has to be submitted by the archaeologist for dating. If we assume that 100 µg of carbon in the form of CO_2 are ideal for a radiocarbon date, and if we are given carbonized plant matter as the sample to be dated, the OAS laboratory has successfully generated datable samples from as little as 200 µg (0.2 milligrams) of parent material (e.g., charred yucca fiber strands; Figure 7). This amount is at the limit of detectability of our laboratory balances. ETH Zurich will process and date samples as small as 10 µg of carbon in the form of CO_2, and extrapolating from the OAS experience with somewhat larger samples, that amount of carbon can be produced from as little as 0.02 milligrams of parent material. Such small samples are at proportionately greater risk of contamination (see below), but they are datable.

Figure 7. Approximately 200 µg (0.2 milligrams) of carbonized yucca fiber. The background for the image is millimeter graph paper, and the sample rests on a porcelain "boat."

Contamination Risk

The surface preference of plasma oxidation makes this type of sampling potentially susceptible to surface contamination. In an effort to assess the nature of this risk, a kiln-cleaned porcelain tile was contaminated by handling with ungloved hands. The contamination test was severe in that the fingers were consciously rubbed over face and scalp to load them with skin oils, but there was no visual evidence of the contamination (no visible fingerprints). After contamination, the tile was broken and one half was placed into a chamber and treated as if it were a sample. After standard argon cleaning plasmas, four rounds of plasma oxidation resulted in the generation of more than 700 µg of carbon from the tile. The second

fragment of the tile was subjected to a standard pH8 cleaning protocol. Because there was no discoloration, the tile was then rinsed with DH_2O and placed in a sampling chamber. There was a dramatic, but not total, reduction in the amount of contamination. A single oxygen sampling plasma resulted in the generation of 70 μg of carbon.

Although we can minimize risk of contamination from OAS laboratory handling of samples prior to plasma oxidation, we cannot know whether contamination has occurred prior to sample submission to the laboratory. That risk cannot be totally eliminated by standard pre-treatment with pH 8, and it remains a problem. In destructive analysis mode, surfaces of samples can be mechanically cleaned by abrading, or slivers of the surface can be removed and old surfaces masked so that only fresh surfaces are exposed to the plasma, but these are only options under conditions of destructive sampling. An alternative pretreatment technique based on cleaning with supercritical fluid may hold the greatest promise and is being investigated (Rowe et al. 2013).

Current Directions

The OAS plasma laboratory can reliably extract radiocarbon samples from a wide variety of materials. At low energies, the plasma oxidation can operate in a virtually non-destructive mode, or high energies can be applied with the result of sampling carbide from historic iron artifacts. However, the plasma oxidation technique raises as many issues as possibilities.

Current research initiatives include:
- *Investigation of supercritical fluid (SCF) as a pretreatment technique to either replace or augment pH 8 rinses.* We have established a research partnership with Los Alamos National Laboratory and will repeat our fingerprint contamination study, attempting to use SCF to remove surface contaminants in controlled settings. SCF will then be used in comparison with pH 8 rinses in a series of paired tests of the pretreatment of archaeological materials for dating.
- *Repeat of studies of powdered alumina as a masking technique using radiocarbon standards to make it easier to detect and quantify any failure of the mask to isolate the "buried" standard from the plasma.* The leakage in the test reported here may be surmountable by compacting the alumina mask using the same application techniques that were developed for the organic pottery paint test reported here.
- *Further exploration of organic paint sampling.* Using independently dated examples of organic-painted pottery, we need to explore the risks of contamination of pottery carbon paint dating by the clay constituents (often carbonaceous Cretaceous shales) of the sherd.
- *Progressive oxidation sampling and dating of rockshelter soot accumulations.* Plasma oxidation has the potential to sample creosote accumulations stratigraphically, segregating recent from old carbon by "planing" carbon from the accumulation at a molecular level. This model will be tested through the creation of soot accumulation standards by anoxic heating of radiocarbon standards of different ages. The creosote-soot evolved will be condensed on cleaned porcelain tiles, creating layers of soot of different (known) ages. This experiment will also allow the development of a model of creosote accumulation on cooking jar sherds that can address the potential of "old wood" in the interpretation of creosote dates.
- *Investigation of variables that influence the plasma sampling and dating of bone.* Attempted dating of bone during the NCPTT grant period failed because of unexplained variability within sample dates and failures to match the consensus dates for international standards. However, the OAS laboratory studies of bone dating took place early in the maturity of our procedures. Improved sample handling protocols and the ability to sample (destructively) the same parent materials with both plasma and acid evolution of CO_2 will allow a much more deliberate

investigation of bone dating. An interesting complication/opportunity is that pH 8 rinsing has also extracted a colloidal like material from some bone during pretreatment, and that material can be dated when concentrated within porcelain boats by evaporation.

- *Further investigation of small samples of different materials.* We are in the early stages of collaborating with fine art conservators in the dating of painting components as an aspect of authentication. This effort is destructive in that we need to physically (and chemically) isolate different painting components (canvas elements, individual pigment colors, etc.) and then collect plasma samples from each component.

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